FOR SN 10/764,704

PTO 09-5754

CC = FR
19681018
B
1542505

HEAT-DEVELOPABLE PHOTOSENSITIVE ELEMENT
[Élément photosensible thermiquement developable]

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JUNE 2009
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	FR
DOCUMENT NUMBER	(11):	1542505
DOCUMENT KIND	(12):	B
PUBLICATION DATE	(43):	19681018 BOPI No. 42
APPLICATION NUMBER	(21):	109314
APPLICATION DATE	(22):	19670606
INTERNATIONAL CLASSIFICATION	(51):	G 03 C
PRIORITY NUMBER	(30):	363871966
PRIORITY DATE	(30):	19660606
PRIORITY COUNTRY	(30):	JP
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TITLE	(54):	HEAT-DEVELOPABLE PHOTOSENSITIVE ELEMENT
FOREIGN TITLE	[54A]:	Élément photosensible thermiquement developable

The object of the present invention is a photosensitive element capable of obtaining images by means of heat.

In general, as a photosensitive element, widespread use has been made of an element in which a silver halide is used, such an element having excellent sensitivity and gradation properties when compared to an electrophotographic photosensitive element, and more generally to other photosensitive elements for photography. However, there are such inherent difficulties in the use of a silver halide photosensitive element that it must be developed in a solution after exposure, and, once developed, the element must be subjected to various operations to prevent the developed image from becoming discolored and faded, and also to prevent the backgrounds from becoming darkened. These various methods are generally referred to as "fixing and stabilizing" in conventional photographic terminology. This is why, from the viewpoint of simplifying the process, it is desirable to obtain an image via dry developing, which obtains a stable image without requiring any fixing operation or the like.

Various efforts have previously been made to obtain such a result. One of them relates to silver halide photography in which developing and fixing are carried out in a fixing and developing bath (according to US 2,875,048, GB 954,453 and DE 1,163,142). Another test was conducted in which the wet process conventionally used in silver halide photography was applied in the dry state, this application being described in DE 1,174,159, GB 943,476 and GB 951,644. Yet another test was conducted in which a silver salt compound other than halide was used, as described in US 3,152,904, BE 663,112 and French Patent Application No. 95,867 dated February 21, 1967.

The present invention relates to an improvement made in the last aforementioned test, which consists of combining a reducible, light-insensitive organic silver salt with a small quantity of light-sensitive silver salt.

Thus, one object of the present invention is to produce a new light-sensitive photographic composition. Another object is to implement a new method of reproducing images. Yet another object of the invention is to produce photosensitive materials which make it possible to obtain both positive and negative copies of an original. Yet another object of the invention is to implement a dry process for carrying out the developing operation exclusively via heat, without making use of any other developing solution.

In addition, one object of the invention is to produce a photosensitive element making it possible to obtain a stable image capable of being preserved nearly intact without having to subject the developed image to fixing or other processes.

Other objects and advantages of the invention will become apparent from the following detailed description.

These objectives are achieved by using a heat-developable photosensitive element consisting of a support receiving at least one layer comprising:

a. A reducible, light-insensitive organic silver salt;

b. An inorganic halide capable of forming a photosensitive silver halide by reacting with the reducible, light-insensitive organic salt a;

c. A reducing agent;

d. An element chosen from the group of organic acids and their salts mixed with a suitable binder.

This heat-developable photosensitive element can be developed by means of heat after exposure, in order to obtain an extremely light-stable image, without having to subject the developed image to other processes such as fixing or stabilization.

The investigations carried out in order to obtain the aforementioned heat-developable photosensitive element led to completing the object of the invention by using a reducing material which loses said

reducing property via irradiation with ultraviolet rays, whereby the reducing agent is decomposed. The reducing agents previously used with heat-developable photosensitive elements are: hydroquinone, methyl hydroquinone, phenyl hydroquinone, catechin and the like, which are not decomposed via ultraviolet ray irradiation.

Thus, the heat-developable photosensitive element in accordance with the invention comprises a support receiving at least one layer containing:

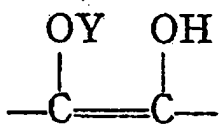
a. A reducible insensitive organic silver salt;

b. An element selected from the group containing a silver halide and an inorganic halide capable of forming a photosensitive silver halide by reacting with the insensitive organic silver salt a;

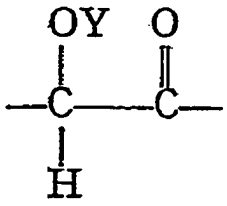
c. A reducing agent capable of being decomposed via ultraviolet irradiation, causing it to lose its reducing property;

d. An organic acid or of a salt thereof.

The reducing agent used in the present invention is a compound containing a chosen element having the generic formula:

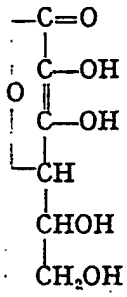


or a compound containing a chosen element having the generic formula:

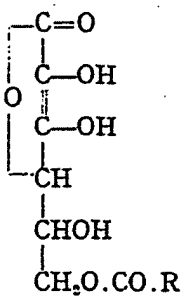


wherein Y represents a hydrogen atom or an acyl group, for example: 1-ascorbic acid (I), 1-ascorbyl monoester (II), 1-ascorbyl diester (III-IV), furoin (V), benzoin (VI), and dihydroxyacetone (VII), the formulas of which are respectively indicated below.

(I)

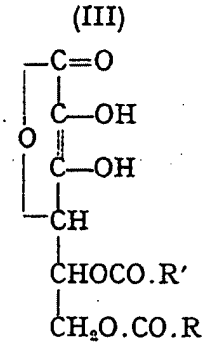


(II)

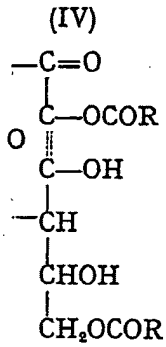


(R represents an alkyl group or an aryl group)

(III)

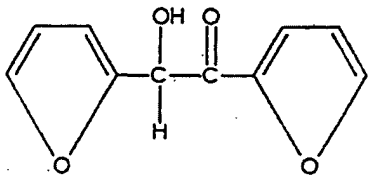


(IV)

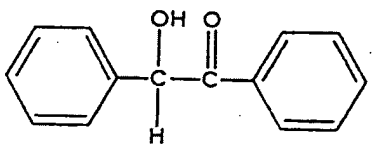


(R and R' each represent an alkyl group or an aryl group)

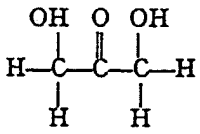
(V)



(VI)



(VII)

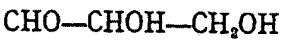


These compounds have the property of losing their heat-developing capacity due to ultraviolet irradiation decomposition.

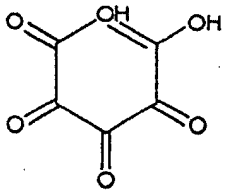
These compounds are known in color photography as antioxidants (US 2,401,713, US 2,728,661, US 2,923,627, GB 922,550), as developing agents for liquid developers (US 2,686,549, GB 430,264), and as preservation agents for liquid developers (Scientific and Technical Photography, No. 81, 1955), but have never been used as heat-developable photosensitive elements.

Finally, it is appropriate to note that the aforementioned compounds are unsuitable for the invention, due to the fact that they do not have the property of being decomposed by ultraviolet irradiation, even though they contain the -C(OH)=C(OH)-or the -CH(OH)-CO group. These are, namely: glyceric aldehyde (VIII), rhodizonic acid (IX) and tetrahydroxyquinone (X), the respective formulas of which are as follows:

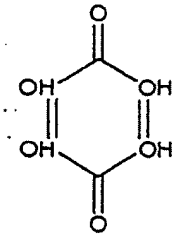
(VIII)



(IX)



(X)



When the reducing agent suitable as a material of the invention, i.e., capable of being decomposed and of losing its capacity to be heat-developed via ultraviolet irradiation, is used as a reducing agent for the heat-developable photosensitive material described in French Patent Application 95,862, dated February 21, 1967, the photosensitive material can be kept in storage for a long time, even under high temperature and high humidity conditions, compared to conventional heat-developable photosensitive materials in which hydroquinone and others are used as reducing agents, and likewise when the material according to the invention is exposed to the light of a tungsten lamp according to the usual method wherein the latent image is developed, and the material is irradiated in order to result in the decomposition of the agent under the action of the ultraviolet rays, or else to the light of a fluorescent lamp in order to cause it to lose its reducing power, the photosensitive material thus obtained produces a very stable image, even if it is exposed to heat or light.

Instead of subjecting the thus exposed and developed photosensitive material to light, it can be subjected to ultraviolet irradiation, which highly ensures the decomposition of the reducing agent. The intensity of ultraviolet exposure required to ensure decomposition of the reducing agent depends on the

proportion of reducing agent contained in the photosensitive material, however, when a 400-watt high-pressure mercury vapor lamp is used, it suffices to expose the developed photosensitive material for 5 min by placing it 10 cm from the source.

A heat-developable photosensitive material such as this, which contains the reducing agent according to the present invention, can likewise be used as an autopositive material. It is in this way that, when the heat-developable photosensitive material of the invention is exposed to ultraviolet radiation through a transparent original, the reducing agent of the surfaces exposed to the ultraviolet rays is decomposed, but the reducing agent of the unexposed surfaces is not decomposed. Consequently, when the photosensitive material exposed to ultraviolet radiation through a transparent original is exposed to a tungsten lamp for a short time and heated, a stable, developed, direct positive image of the original is obtained, thereby establishing that the photosensitive material of the invention is usable as an autopositive material.

As a light-insensitive silver salt used in the invention, mention may be made of: the silver salts of organic compounds that have an imino group, such as a substituted silver salt of benzotriazole or a silver salt of methyl halogen and nitrobenzotriazole and a silver salt of saccharin, as described in FR 1,512,080, dated February 21, 1967, and also the silver salts of organic compounds having a carboxyl group, such as silver behenate.

The inorganic halide capable of forming a silver halide by reacting with the light-insensitive silver salt is a compound that is soluble in water or in an organic solvent, having the generic formula MXn, wherein M is hydrogen or ammonium, or a metal such as strontium, cadmium, zinc, tin, chromium, sodium, potassium, barium, iron, cesium, lanthanum, copper, calcium, nickel, magnesium, aluminum, antimony, gold, cobalt, mercury, lead or beryllium; X being a halogen such as chlorine, iodide or bromine, and n being the valence of M.

As an organic acid used in the invention, mention may be made of: saturated aliphatic monocarboxylic acids with 9-26 carbon atoms, e.g., such as pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid and cerotic acid. Among these, those with 12-22 carbon atoms are particularly preferable, the preferred one is lauric acid, which has 12 carbon atoms, or myristic acid, which has 14, or palmitic acid, which has 16, or stearic acid, which has 18, or arachidic acid, which has 20, or behenic acid, which has 22.

Aliphatic dicarboxylic acids with 4-10 carbon atoms are used in the invention, such as: succinic acid, glutaric acid, adipic acid, sebacic acid, etc.

The proportion of reducing agent is generally determined by the reducing power, the rate of the decomposition of same under light and the molecular weight of the compound used. In general, it is preferable to use the reducing agent in a proportion of 1/100 to 10 parts by weight, to one part by weight of the light-insensitive silver salt. The proportions of the other constituents are the same as those which were provided in French Patent Application 95,862, i.e., they are from 1/10 to 1/100,000 for material b, from 1/100 to 10 parts for material d, in a mixture with 1/10 to 20 parts by weight of a suitable binder.

The following examples introduce the preferred preparation methods for producing heat-developable photosensitive elements in accordance with the invention.

Examples 1-7

In each example, a uniform dispersion with the composition shown in Table 1 is prepared; the heat-developable photosensitive element obtained results from the application of this dispersion to a photographic paper, at a dry layer thickness of 15 μm; the photosensitive material thus produced is heated in order to produce a negative image after exposure under a tungsten lamp. When the negative image thus obtained is exposed to light, the contrast between the image surfaces and the background

surfaces of the material does not undergo any variation. On the other hand, when the heat-developable photosensitive material thus prepared is exposed for 5 min to a 400-watt high-pressure mercury vapor lamp and heated by placing it 10 cm from the source as indicated in the table, a good positive image is obtained. When the image thus obtained is exposed to white light, the contrasts in density between the image surfaces and the background surfaces of this material are unchanged.

	Example No.						
	1	2	3	4	5	6	7
Polyvinyl butyral (10% solution in methanol) mL	60	60	60	60	60	60	45
Silver salt of benzotriazolyl (10% dispersion in methanol) mL	15	20	20	20	-	-	-
Silver salt of saccharin (10% dispersion in methanol) mL	-	-	-	-	-	20	-
Silver behenate (10% dispersion in methanol) mL	-	-	-	-	20	-	40
Strontium iodide (1/50 N solution in methanol) mL	15	10	10	10	-	10	-
Potassium iodide (1/50 N solution in methanol) mL	-	-	-	-	10	-	25
Sensitizing dye (1) 0.25% solution in methanol) mL	0.4	0.4	0.4	0.4	0.4	0.4	1
1-ascorbic acid (in g)	0.2	-	-	-	-	-	-

1-ascorbyl palmitate (in g)	-	0.1	-	0.2	-	-	0.25 and 1
1-ascorbyl laurate (in g)	-	-	0.1	-	0.2	-	-
1-ascorbyl myristate (in g)	-	-	-	-	-	0.1	-
Sebacic acid (in g)	-	-	4	2	-	-	4
Adipic acid (in g)	2	2	-	-	3	-	-
Heating time to obtain a negative image from an original (in seconds)	5	5	10	1	5	5	10
Temperature (in °C)	120	120	110	160	140	120	110
Heating time to obtain a positive image from a negative original (in seconds)	5	5	10	1	5	5	10
Temperature (in °C)	120	120	110	160	140	120	110
(1) Composition of the sensitizing dye: 2-ethyl-5-[(3-methyl-2-thiazolinilidene)-ethylidene]-rhodamine							

Examples 8-10

Each of the dispersions with the compositions indicated in the Table below was applied to a photographic paper and dried, the dry thickness of the application being 15 μm.

	Example No.		
	8	9	10
Polyvinyl butyral (10% solution in methanol) mL	60	60	60
Silver salt of benzotriazolyl (10% dispersion in methanol) mL	20	20	20
Silver behenate (10% dispersion in methanol) mL	-	-	-

Strontium iodide (1/50 N solution in methanol) mL	10	10	10
Potassium iodide (1/50 N solution in methanol) mL	-	-	-
Sensitizing dye (1) (the same as above) (0.25% solution in methanol) mL	0.4	0.4	0.4
Furoin (in g)	3	-	-
Dihydroxyacetone (in g)	-	3	-
Benzoin (in g)	-	-	0.3
Adipic acid (in g)	2	2	-
Sebacic acid (in g)	-	-	4

When these various examples are exposed under a tungsten lamp, as in Example 1, good negative images are obtained, and when these various examples are exposed under a mercury vapor lamp, good positive images are obtained. When the images are exposed to white light, the contrast in density between image and background is unchanged.

Claims

The object of the inventions is:

1. A heat-developable photosensitive element comprising a support to which at least one layer is applied, which contains:

a. A reducible, light-insensitive organic silver salt;

b. An element selected from the group containing a silver halide and an inorganic halide capable of forming a photosensitive silver halide by reacting with the insensitive organic silver salt a;

c. A reducing agent capable of being decomposed via ultraviolet irradiation, causing it to lose its reducing property;

d. An organic acid or of a salt thereof.

2. The heat-developable photosensitive element according to Claim 1, wherein the reducing agent is selected from the group having the generic formulas: -C(OY)=C(OH) and -CH(OY)-CO- wherein Y represents a hydrogen atom or an acyl group.

3. The heat-developable photosensitive element according to Claim 1, wherein the reducing agent is selected from the group consisting of: l-ascorbic acid, l-ascorbyl monoester, l-ascorbyl diester, furoin, benzoin, and dihydroxyacetone.

4. The heat-developable photosensitive element according to Claim 1, wherein the reducible insensitive organic silver salt is a silver salt of an organic group having an imino group.

5. The heat-developable photosensitive element according to Claim 4, wherein the organic group having an imino group is chosen from among the groups consisting of silver benzotriazyl or a silver salt of saccharin.

6. The heat-developable photosensitive element according to Claim 1, wherein the reducible insensitive organic silver salt is a silver salt of an organic group having a carboxyl group.

7. The heat-developable photosensitive element according to Claim 6, wherein the silver salt of the organic compound having a carboxyl group is silver behenate.

8. The heat-developable photosensitive element according to Claim 1, wherein said organic acid is chosen from among aliphatic monocarboxylic acids with 12-22 carbon atoms or aliphatic dicarboxylic acids with 4-10 carbon atoms.

9. The photosensitive element according to Claim 1, wherein said inorganic halide capable of forming a light-insensitive silver salt is a compound with the generic formula MXn, wherein M is

hydrogen, strontium, cadmium, zinc, tin, chromium, sodium, nickel, magnesium, aluminum, antimony, gold, cobalt, mercury, lead or beryllium, or else an ammonium group, said X being a halogen, and said n being the valence of M.

10. Method for obtaining a stable negative print from an original, comprising the exposure of a heat-developable photosensitive element according to Claim 1 to light while heating said element for 1-10 sec at a temperature of 110-160°, and while exposing it either to sunlight or light from a fluorescent lamp or a mercury lamp.

11. Method for obtaining a stable positive print from an original, comprising the exposure of a heat-developable photosensitive element according to Claim 1 to ultraviolet radiation while heating said material for 1-10 sec at a temperature of 110-160°.